

## CARBON CATALYSTS FROM COAL FOR ENVIRONMENTALLY RELEVANT REACTIONS

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### INTRODUCTION

Activated carbons can be produced from coals by a variety of thermal and chemical-thermal methods. A method related to the present paper is the chemical treatment of coal with aqueous KOH first at relatively low temperature (315-482 °C), followed by carbonization at higher temperatures in the range of 704-982 °C (1). In previous publications (2-4) we have shown that temperatures as low as 75 °C in the first step, followed by carbonization at 600-900 °C gave good quality, high surface area, active carbons.

Activated commercial carbons produced from coal are used for water purification, solvent recovery, supports for catalysts (5) and for SO<sub>x</sub> and NO<sub>x</sub> removal from gas streams (6).

Another important use of carbon catalysts for environmental cleaning is the removal of halogen from halogen-containing compounds. Two basic approaches could be used: 1. gas phase catalyzed oxidation of the halogen-containing compounds to carbon dioxide and the corresponding halogen-containing acid (7) and 2. catalytic dehalogenation. The case of carbon catalyzed dehalogenation of an alkyl chloride was studied in detail by Sohr and Boehm (8). The case of liquid-phase carbon black catalyzed hydrodehalogenation of halogenated aromatic compounds was studied by Farcasiu et. al (9,10). An important difference between the oxidative dehalogenation and hydrodehalogenation is that in the oxidative method the carbon in the halogen-containing compounds is transformed into carbon dioxide, while in hydrodehalogenation the halogen removal from an aromatic hydrocarbon is selective and the hydrocarbon skeleton is maintained. The two methods address two different environmental situations, i.e. the removal of a high concentration contaminant (oxidation), or the selective removal of halogen from a hydrocarbon mixture containing some halogen compounds.

The use of carbon materials such as some carbon blacks, for hydrodehalogenation and hydrodehydroxylation of condensed polyaromatic compounds has been reported (9,10). Very good activities and selectivities have been observed with some carbon blacks for the hydrodehalogenation of halogenated condensed polyaromatic compounds such as halogenated naphthalenes, phenanthrenes, and pyrenes. Only very modest dehalogenation was observed for compounds, such as 4-chlorobiphenyl, containing halogen substituted at benzenic rings.

When carbon materials are used as catalysts for specific reactions, the preparation of the carbon material could be customized to substantially increase in the catalytic activity. The role of the carbonization temperature on the catalytic activity (for hydrocracking of alkyl substituted condensed polyaromatics) of resorcinol-formaldehyde aerogel-based materials has been reported (11). In that work it was shown that the catalytic activity of the carbonized aerogels increases with the carbonization temperature, reaches a maximum around 1050 °C and then decreases dramatically. Graphite is not active catalytically in such hydrocracking reactions.

We have found that under very defined preparation conditions, carbon materials prepared from coal could be very active hydrocracking and hydrodehalogenation catalysts for aromatic compounds. We reported recently (12) the influence of the method of preparation on the catalytic activity of coal-derived carbon catalysts for hydrocracking and hydrodehydroxylation reactions.

In the present publication, we will discuss how various parameters could be varied during

the preparation of coal-based catalysts to optimize their activity for the dehalogenation reaction of halogenated aromatic compounds.

## EXPERIMENTAL

Various coals were activated using a two step procedure at the Center for Applied Energy Research (2). The first step involved the mixing of a solution of potassium hydroxide with -100 mesh cleaned coal (KOH to coal weight ratio 1.42:1). This mixture was heated at 75 °C for two hours under nitrogen. The heat treatment temperature (HTT) at 800 °C or 900 °C for one hour is the second step, followed by leaching to remove KOH.

Indiana VII is a hvC bituminous coal and was cleaned at Entech Global, Inc, using two different methods. Selective agglomeration (SA) is a method for rejecting mineral impurities from ground coal using pentane and heptane as reusable bridging liquids. Microcel™ Column (MC) is a column flotation method. Wyodak Black Thunder is a subbituminous coal, and Illinois Basin hvC coal (IBC) is a high volatile, bituminous coal.

The surface areas of these activated carbons were measured by nitrogen adsorption at 77 K using the BET method.

Two activated carbons, WS 4 and Centaur™ HSV, were donated by Calgon Carbon Corporation. The WS 4 carbon is prepared from dense wood and thermally activated, while Centaur™ HSV is prepared from bituminous coal. A carbon black, Black Pearls 2000 (BP2000), was donated by Cabot Corporation.

The dehalogenation activity of various carbon catalysts was tested for the debromination of 1-bromonaphthalene in the presence of a hydrogen donor, 9,10-dihydrophenanthrene (9,10-DHP). The reaction conditions were in all cases: 350 °C, 1 hour, wt. ratio 1-bromonaphthalene : 9,10-DHP : catalyst 1 : 4 : 0.1. The experimental procedure is explained elsewhere (9).

Gas chromatographic analysis of the product was carried out on a Hewlett Packard 5890A Series II, equipped with a JW-SE-42 column and a FID.

## RESULTS AND DISCUSSION

We observed previously (9,12) that the reaction-specific catalytic activity of some synthesized carbon catalysts could be optimized by varying the preparation conditions. We observed that the preparation is reaction-specific and chemical reactions with various mechanisms could require quite different carbon materials to achieve optimum catalytic activity. We believe this fact is related to the presence of several types of active sites on the surface of the catalyst and to their relative concentration and/or strength, as a function of the preparation conditions. We will discuss how such a preparation could be optimized for the dehalogenation of halogenated condensed polyaromatic hydrocarbons. The method for the synthesis of coal-based carbon catalysts is described in the experimental part. Several parameters are very important in the preparation of coal based catalysts according to this method:

1. the temperature of step 2 (HTT)
2. the rank of coal
3. the method of coal preparation/cleaning prior to activation

### 1. Influence of the temperature in step 2 (HTT)

We have found that catalysts for hydrodebromination and hydrodehydroxylation reactions can be made by chemically activating coals (Table 1). These activated carbons perform better than commercially available carbon materials such as BP2000 (Cabot), WS 4 and Centaur™ HSV (Calgon). As shown in Table 1, the extent of the hydrodebromination of 1-bromonaphthalene is greatest when the heat treatment temperature (HTT) in step 2 reaches 800 °C. At this temperature, surface area is at a maximum, but as can be observed from the conversion data, the increase in surface area alone cannot explain the difference in reactivity. In the case of the hydrodehydroxylation of 2-naphthol, the maximum conversion is reached at 700 °C and appears to become steady above that temperature. For comparison we show data (Table 1) on the catalytic activity of some commercial active carbons. BP2000 and WS 4 are nearly the same for both reactions. However taking into account the higher surface area of BP2000, WS 4 appears to be a

slightly more active catalyst. Centaur™ HSV, which is made from bituminous coal, is the least active in our reactions.

The products in the hydrodebromination reaction are tetralin, naphthalene, and 2-bromo-5,6,7,8-tetrahydronaphthalene. The hydrodehydroxylation reaction yields tetralin, naphthalene, naphthalone, and 2-hydroxy-5,6,7,8-tetrahydronaphthalene.

The influence of HTT in step 2, was also observed for Indiana VII activated carbons in Table 2.

## 2. Influence of coal rank

We found that a HTT of 900 °C is optimal for both Indiana VII bituminous coal and Black Thunder subbituminous coal in the hydrodehalogenation of 1-bromonaphthalene. However, if we compare the highest hydrodehalogenation values, the catalyst prepared from subbituminous coal is better than the catalyst prepared from bituminous coal. Under our test conditions, the best catalyst obtained from Indiana VII gave a conversion of 1-bromonaphthalene of 62% as compared with 76% for the best preparation from Black Thunder subbituminous coal. Whether these results represent the general case, and better catalysts for the debromination can be obtained from subbituminous coals, is far from being proven and therefore more cases should be studied.

## 3. Influence of the method of coal cleaning on the catalytic activity of the carbon catalysts

To avoid a large concentration of mineral matter in the activated carbons prepared from coals, the coal mineral matter should be substantially removed prior to activation. We started a systematic study in this area using Indiana VII precleaned by Entech to about 2.6 % ash by two different cleaning methods: solvent agglomeration and column flotation (see the experimental section). Cleaning the same coal using a dry separation method (tribo-electrostatic separation) is in progress, and the coal obtained by this method will be also used to prepare carbon catalysts. The results obtained to date are given in Table 2.

The data (Table 2) seem to indicate that coal cleaning by aqueous flotation (MC) in the presence of low amounts of surfactants is a preferred method to clean coals prior to synthesis of the catalysts. It may be that the coal cleaning method influences the types of active sites present on the surface of carbon catalysts, and therefore it may be possible to control the selective catalytic properties by choosing the conditions of the catalyst preparation.

## CONCLUSIONS

Carbon materials prepared from coals could be used as active and selective catalysts for reactions of interest in environmental chemistry, such as the dehalogenation of halogenated condensed polyaromatics and the dehydroxylation of phenols or condensed polyaromatics. We have identified three important parameters to be considered in the catalyst preparation: 1. the temperature of step 2 (HTT); 2. the rank of coal; 3. the method of coal preparation/cleaning prior to activation.

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## DISCLAIMER

Reference in the paper to any specific commercial product, process, or service is to

facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy.

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Table 1. Effect of Heat Treatment Temperature (HTT) on Hydrodehalogenation and Hydrodebromination Reactions.

CATALYST	HTT °C	SURFACE AREA m <sup>2</sup> /g	% CONVERSION <sup>1</sup>	
			1-Br-naphthalene	2-Naphthol
IL #6 IBC 106	600	835	26	35
IL #6 IBC 106	700	1081	40	48
IL #6 IBC 106	800	1583	72	48
BP-2000	-----	1475	25	36
WS4	-----	1300	22	34
CENTAUR™ HSV	-----	-----	8	20

1. Wt ratio Catalyst:1-Br-naphthalene or 2-naphthol:9,10-DHP=1:10:40; reaction temperatures for 1-Br-naphthalene or 2-naphthol are 350 °C and 410 °C, respectively , for 1 hour.

Table 2. Effects of Coal Cleaning Methods on the Conversion of 1-Br-naphthalene.

COAL <sup>1</sup>	HTT °C	SURFACE AREA m <sup>2</sup> /g	% CONVERSION <sup>2</sup>
Indiana VII-SA	800	1602	50
Indiana VII-SA	900	2180	59
Indiana VII-MC	800	1790	57
Indiana VII-MC	900	1997	69

1. SA=Selective Agglomeration; MC=Microcel™ Column.

2. Catalyst:1-Bromonaphthalene:9,10-DHP = 1:10:40 at 350 °C for 1 hour.